

4. Discussion

Over the years, the corrosion performance of carbon steel and low-alloy steel in boric-acid-containing aqueous environments has been studied by several investigators. Boric acid crystals have been observed at several locations in several pressurized water reactors in which the coolant contained nominally 1000 ppm B as boric acid and 2 ppm Li as lithium hydroxide. Solid boric acid crystals by themselves have been of little concern from the corrosion standpoint of ferritic steels; however, the presence of water/moisture and oxygen can lead to enhanced corrosion of ferritic steels, especially at elevated temperatures. For example, highly concentrated solutions of boric acid, albeit locally, can increase the H ion concentration (decrease the pH) in the solution and make the environment more acidic (see Figure 9c), even though boric acid by itself is considered a weak acid when compared with hydrochloric or nitric acids.

Studies have been conducted to evaluate the uniform wastage of carbon and low-alloy steels in simulated environments with emphasis on evaluation of the role of key variables such as temperature, boric acid concentration, flow velocity, specimen/crevice geometry, aeration/deaeration, etc., in corrosion.

The Electric Power Research Institute (EPRI) conducted a series of tests in which carbon and low-alloy steel specimens were buried in boric acid crystals at room temperature and exposed to water saturated flowing air for 60 days. They concluded that the average corrosion rates for the steels were 0.001-0.005 mm/y.¹²

The Moscow Power Institute conducted a series of tests by immersing plate-type carbon steel specimens in aerated and deaerated borated water for up to 1000 h. They reported long-term corrosion rates of 0.005 mm/y in aerated water with 3000 ppm B at 310°C and 0.008 mm/y in aerated water with 1000 ppm B at 200°C.^{13,14}

Combustion Engineering conducted a series of tests with unclad SA-533 Grade B steels (among others) by immersing them in an autoclave with deionized, aerated water and 723 ppm B, 1.8 ppm Li, and 0.4 ppm ammonia.¹⁵ The specimens were held at 176°C for 70 h. They reported an average corrosion rate of 0.41-0.43 mm/y. Brookhaven National Laboratory conducted tests on several carbon and low-alloy steels at 100 and 178°C in aerated water containing 4000 ppm B and LiOH at a pH of 7.3.¹⁶ The study reported rates of 1.2-1.4 and 2.8-3.3 mm/y at 178 and 100°C, respectively.

Westinghouse performed immersion and dripping tests on low-alloy steel in aerated and deaerated boric acid solutions.¹⁷ The test solutions were identified as 15 and 25%. The solutions were termed “aerated,” if they were left open to air during the exposure of the test specimens. The solutions were termed “deaerated,” if the system was closed and the oxygen in solution was assumed consumed by the test specimens. No direct measurements were made of the oxygen content of the solutions. The study reported corrosion rates of 122 and 76 mm/y at 93°C for low-alloy steel immersed in 25% solution in aerated and deaerated conditions, respectively. Westinghouse also reported corrosion rates in the range of 4.2-4.8 mm/y at 99°C for steel dip tested in air in a 15% solution of boric acid. Results from this study indicate that the presence of oxygen and high concentrations of boric acid in an aqueous solution can lead to very high corrosion rates for the low-alloy steel. Furthermore, the so-called “deaerated”

condition decreases the rate from 122 to 76 mm/y ($\approx 38\%$). The rate still seems high indicating the possibility that the oxygen level may not be as low as one would expect under deaeration achieved by bubbling of hydrogen gas. The data also indicate that corrosion rates for the low-alloy steel are of similar magnitude, when exposed in immersion or in dip tests. Westinghouse also reported no corrosion of carbon steel specimens when exposed to dry boric acid crystals at 260°C.

Combustion Engineering also conducted immersion experiments with carbon and low-alloy steels in aerated solutions with B concentrations of 22,000 ppm and saturated value ($\approx 40,000$ ppm) at 104°C.^{16,18} In these experiments they immersed plate-type specimens of SA-533 Grade B (among others) in a flask with water-cooled condensers at the top to prevent evaporation of the test solutions. Specimens were removed at various intervals to determine the corrosion progress with time and to evaluate the corrosion rates. Combustion Engineering reported corrosion rates of 16.5 and 9.1 mm/y after 24 and 96 h exposures in a solution containing 22,000 ppm B and a pH of 3.0. The rates were 36.1 and 7.6 mm/y after 6- and 27-h exposures in a solution containing 26,200 ppm B and a pH of 4.0. Combustion Engineering did not report data for low alloy steel in the B-saturated solution, but reported a corrosion rate (based on a 4-h exposure) of 184 mm/y for SA-106 Gr B carbon steel. These results indicate that the initial corrosion rates are, in general, higher than those based on long time exposures. Combustion Engineering also reported that the corrosion rate differences between different ferritic steels (SA-106, SA-533, and SA-508) were small, when tested in a given environment. The study attributed the reduction in the average corrosion rate with increasing test duration to lack of replenishing of the solution during the test, since the pH changed from 3-4 at the start of the test to 5-6 at the end of testing. The study concluded that replenishing the solutions, as is the case with many leaking joints, would have increased the corrosion rates.

Babcock and Wilcox also conducted four tests to evaluate the corrosion of carbon steel in a boric acid environment using a test apparatus that consisted of a 0.9-m-long steel pipe supported at a 30° angle from the horizontal.¹⁹ The pipe was heated from the inside to 260-288°C, and 0.6 m of the pipe was covered by insulation that was separated from the pipe surface by a 19-mm annulus. Simulated primary water (borated and lithiated) at 93°C was then dripped onto the exposed surface of the pipe at three locations. The boric acid concentration was 13,000-14,300 ppm (2270-2500 ppm B), and the Li concentration was 1.3-1.7 ppm. The test duration ranged between 198 and 263 h. The dripped water evaporated as it was heated by the hot pipe surface, which led to an increase in boric acid concentration. At the completion of the tests, the pipes were cut and analyzed to obtain corrosion depths. The highest corrosion rates in the four tests were 102-198 mm/y and the lowest rates ranged between 0 and 7.7 mm/y. The study concluded that corrosion rates can be as high as 76-127 mm/y at downstream locations where cold borated water drips directly onto carbon steel surfaces, and that the rates can be even higher where boric acid condenses on metal surfaces near 93°C.

Recently, corrosion rate data were obtained at 100°C by Arioka* on alloys containing 4, 8, 11.5, and 15 wt.% Cr in deaerated aqueous solutions containing boric acid concentrations of

*Private communication from R. W. Staehle to W. H. Cullen (USNRC), forwarded to K. Natesan (ANL) and also from K. Arioka (Japan) to J. H. Park (ANL).

7,000, 21,000, and 38,000 ppm B. Section loss calculated from the weight change data showed corrosion rates of 6.1, 31.5, and 114 mm/y for an alloy containing 4 wt.% Cr.

Several conclusions can be drawn from the results presented above from various studies:

- Corrosion of low-alloy steel is minimal when the steel is exposed at room temperature to solid boric acid crystals even in the presence of flowing humid air (Southwest Research study)¹² or when exposed to dry boric acid crystals at 200°C (Westinghouse study).¹⁷
- Presence of boric acid at high concentrations in aerated aqueous solutions can increase metal wastage in ferritic steels such as carbon steel and low-alloy steels.
- Results from the BNL study¹⁶ showed corrosion rates of 2.8-3.3 and 1.2-1.4 mm/y at 100 and 178°C, respectively, in aerated solutions with 4000 ppm B and LiOH.
- Increasing the boric acid concentration to 25% in solution (\approx 9,000 ppm B) resulted in corrosion rates of 122 and 76 mm/y at 93°C under aerated and deaerated conditions, respectively, (Westinghouse study).¹⁷
- Corrosion rates are similar for ferritic steels exposed to boric acid solutions, irrespective of whether the specimen is immersed in the solution or the boric acid solution is dripped onto the specimens.
- There is very little quantitative corrosion rate information in the temperature range of \approx 100-250°C in solutions that contain a wide range of boric acid concentrations.
- There is a lack of corrosion information in molten salt type environments that are potentially feasible in H-B-O system at intermediate temperatures.
- There is a lack of corrosion information in high-pressure, high-temperature boric-acid containing environments.

The overall objective of the ANL program was to conduct research in specific areas focused to determine the conditions that can lead to aggressive and rapid rate of attack of pressure vessel steel in the presence of high concentrations of boric acid in nuclear power plants. For this purpose, the ANL study was conducted in three different and distinct environmental conditions to understand the corrosion performance of reactor steels exposed to H-B-O system.

The three environments used in the study are 1) room-temperature saturated boric acid solution in aerated and deaerated conditions for ECP and corrosion experiments at 95°C, 2) molten-salt solutions with and without water additions for corrosion tests at 150-320°C, 1 atm, and 3) high-pressure (12.4 MPa) high-temperature (up to 316°C) water with a range of boric acid solution concentrations for ECP and corrosion experiments.

- The selected environments address the following scenarios:

Low leakage, nozzle/annulus open: water flashes, leaving boric acid deposits on RPV head surfaces at $>300^\circ\text{C}$; high-temperature molten salt solutions at ambient pressure with or without moisture.

Low leakage, nozzle/annulus plugged: similar environment on both sides of the nozzle; high-temperature high-pressure PWR environment with varying boron and lithium content.

Higher leak rate (≈ 0.1 gal/min) & nozzle/annulus open: heat of evaporation provides cooling; low-temperature saturated boric acid solutions concentrated through boiling & enhanced by oxygen from ambient atmosphere.

- The study showed corrosion rates of 40 mm/y for A533 Gr.-B low-alloy steel at 97.5°C when tested in room-temperature saturated boric acid solution. The rates in half-saturated solution were a factor of 2 lower than in saturated solution. The rates in deaerated solutions were half as much as in aerated solutions for a given boric acid concentration.
- No corrosion was observed in any of the alloys (including A533 steel) in molten H-B-O salt when moisture was not present.
- Very high corrosion rates were observed for the A533 steel at 140-170°C in super saturated H-B-O solutions when water was added. Rates up to 150 mm/y were measured at 150°C (Figs. 47 and 48).
- The corrosion experiments in high temperature-high pressure water containing 4,000 and 9,090 wppm B showed rates of <0.1 and 8 mm/y at temperatures of 316 and 100°C, respectively (Fig. 49).

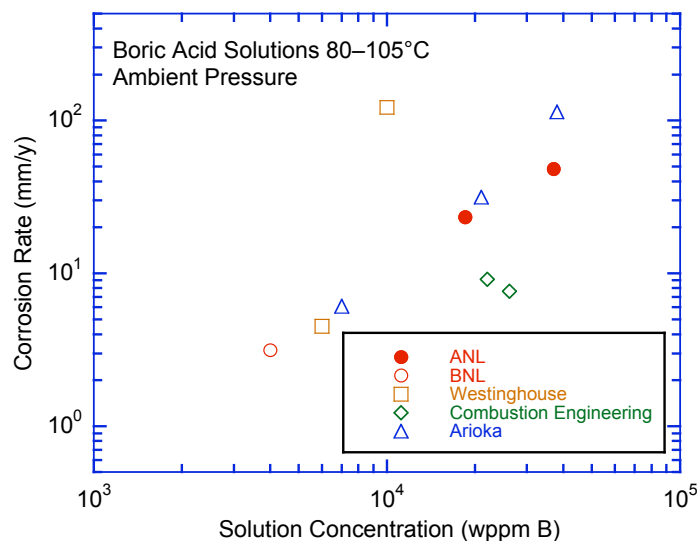


Figure 47.
Measured corrosion rates for low-alloy steels in various solutions of boric acid at 80-104°C and ambient pressure.

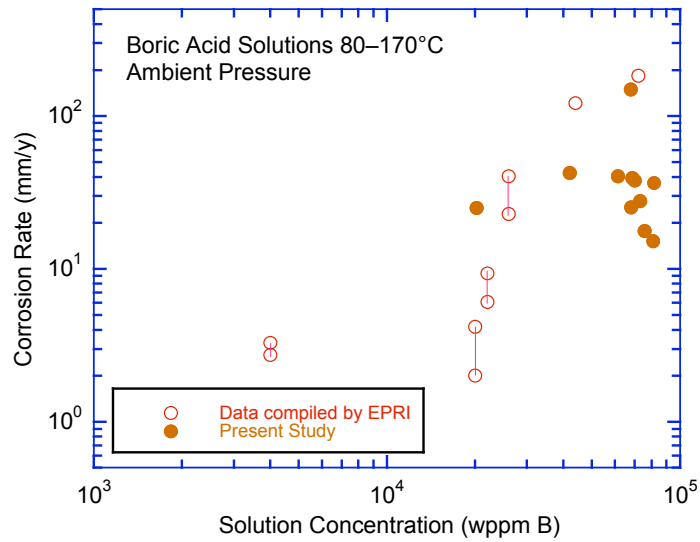


Figure 48.
Measured corrosion rates for low-alloy steels in various solutions of boric acid at 80–170°C and ambient pressure.

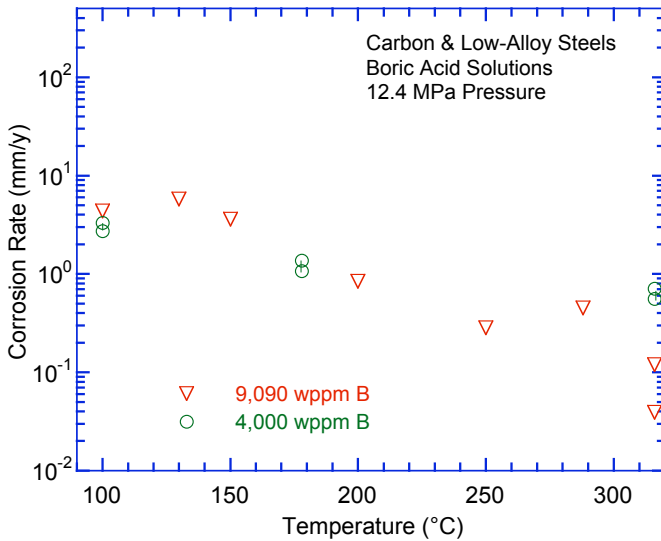


Figure 49.
Measured corrosion rates for carbon and low-alloy steels in boric acid solutions at 12.4 MPa pressure.

5. Summary

This report presents experimental data on ECP and corrosion/wastage rates for the materials found in the RPV head and nozzles of a typical PWR in boric acid solutions of varying concentrations at temperatures of 95–316°C (203–600°F). Tests were conducted in environmental conditions that have been postulated in the CRDM nozzle/head crevice: (a) high-temperature, high-pressure aqueous environment with a range of boric acid solution concentrations; (b) high-temperature (150–300°C) boric acid powder at atmospheric pressure with and without the addition of water; and (c) low-temperature ($\approx 95^\circ\text{C}$) saturated boric acid solutions both deaerated and aerated. These environmental conditions correspond to the following situations: (a) low leakage through nozzle crack and nozzle/annulus plugged, (b) low leakage through nozzle crack and nozzle/annulus open, and (c) significant cooling due to high leakage through nozzle crack and nozzle/annulus open.

Test facilities were assembled to perform ECP and corrosion rate measurements on A533 Gr.-B low-alloy steel, Alloy 600, and 308 SS weld clad, in the various postulated environments in the CRDM nozzle/head crevice. In general, the ECP of all alloys decreased with an increase in temperature. At temperatures below 150°C the ECP of A533 Gr.-B low-alloy steel was significantly lower than that of the other alloys. Also, at 95°C, the ECP of A533 Gr.-B steel decreased slightly as the concentration of boric acid in the solution was decreased from 36,000 ppm to 3,500 ppm. At 150–316°C and 12.4 MPa (1800 psi) pressure, the ECP of all alloys were comparable in PWR water with 1000 or 9090 ppm B, ≈ 2 ppm Li, <10 ppb DO, and ≈ 2 ppm dissolved hydrogen.

In the various environments investigated in the present study, the corrosion rates of Alloy 600 and 308 SS cladding were found to be negligible compared to those of A533 Gr.-B steel. Also, in the absence of moisture, no corrosion was observed for any of the materials in H-B-O environments at 150, 260, and 300°C; the H-B-O environments consist of a dry powder of $\text{HBO}_2 + \text{H}_3\text{BO}_3$ at 150°C, molten HBO_2 at 260°C, and molten mixture of $\text{HBO}_2 + \text{B}_2\text{O}_3$ at 300°C.

For A533 Gr.-B steel, an average corrosion rate of ≈ 40 mm/y (1.6 in./y) was measured in aerated saturated solution of boric acid at 97.5°C and ambient pressure. The corrosion rate in aerated half-saturated solution was a factor of ≈ 2 lower than in saturated solution; the rates for deaerated solution were $\approx 40\%$ lower than in aerated solution. Very high corrosion rates were observed for A533 Gr.-B steel at 140–170°C in super-saturated molten salt solutions of boric acid with addition of water. Short-term corrosion rates up to 150 mm/y were measured at 150°C.

The corrosion experiments in high-temperature high-pressure water containing 9090 ppm B, ≈ 2 ppm Li, <10 ppb DO, and ≈ 2 ppm dissolved hydrogen showed that the corrosion rates decreased with increasing temperature. The rates were ≈ 5 mm/y at 100–150°C and decreased to <0.1 mm/y at 316°C.

The existing corrosion/wastage data in boric acid solutions in the literature have been summarized. The earlier studies, predominantly conducted at 80–104°C, showed that the corrosion rates for low-alloy steel can increase from ≈ 3 mm/y to greater than 100 mm/y as the B concentration in the solution was increased from $\approx 4,000$ to 40,000 wppm. The results from

the present study in saturated boric acid solutions at 97.5°C are in agreement with the earlier data. In addition, very high corrosion rates were observed for low-alloy steel at 140–170°C in molten salt solutions of boric acid with addition of water. Short-term corrosion rates up to 150 mm/y were measured at 150°C, which are in the same range that was observed in saturated boric acid solutions at 97.5°C. The corrosion rate data developed over a wide temperature range in the present study may be used to assess the corrosion performance of the RPV and CRDM nozzle materials in boric acid solutions.

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11. ABSTRACT (200 words or less) This report presents experimental data on electrochemical potential and corrosion rates of the materials found in the reactor pressure vessel head and control rod drive mechanism (CRDM) nozzles in boric acid solutions of varying concentrations at temperatures of 95–316°C (203–600°F). Tests were conducted in postulated environmental conditions in the nozzle/head crevice, e.g., (a) high-temperature, high-pressure aqueous environment with a range of boric acid solution concentrations, (b) high-temperature (235–320°C) molten salt solutions, and (c) low-temperature (≈95°C) saturated boric acid solutions. These correspond to the following situations: (a) low leakage through the nozzle and nozzle/head annulus plugged, (b) low leakage through the nozzle and nozzle/head annulus open, and (c) significant cooling due to high leakage and nozzle/head annulus open. The results indicate significant corrosion only for the low-alloy steel and no corrosion for Alloy 600 or 308 stainless steel cladding. Also, corrosion rates were significant in saturated boric acid solutions, and no material loss was observed in boric acid melts or deposits in the absence of moisture. The results are compared with the existing corrosion/wastage data in the literature.					
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